"A new way of looking at the Rapid Chloride Permeability Test".

Peter Claisse, Coventry University, Priory Street, Coventry CV1 5FB, UK
p.claisse@coventry.ac.uk
+44 2476 888881

The "Rapid Chloride Permeability Test" in ASTM C1202 is well known for not being rapid, not primarily measuring chlorides and not measuring permeability. Nevertheless it is a very useful test that has gained significant acceptance in the USA and is now being used increasingly in Europe. This paper will include results from a new computer model of the test which illustrates some of the physical processes that it does measure (electromigration and diffusion of hydroxyl, chloride and other ions). The model also predicts the voltage drop across the sample and shows that this is often highly non-linear. Initial observations of the non-linearity will be presented and the effect of the resulting changes in the electric field on modelling the test will be discussed. The paper will conclude with recommendations to improve the use and interpretation of the test.

1. Introduction

The Rapid Chloride Permeability Test (RCPT) was developed by Whiting (1) and has been standardised as ASTM C1202-97 (2). The test procedure is shown in figure 1.

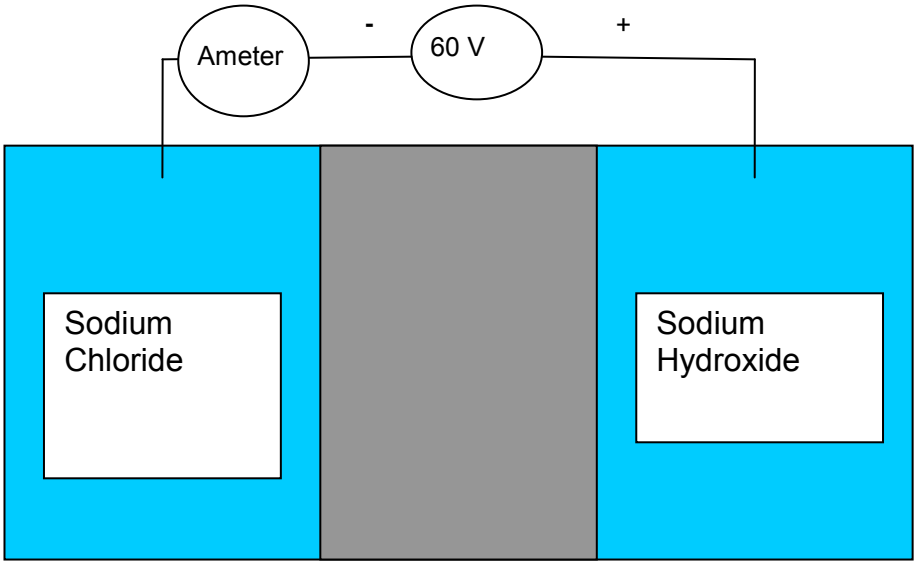


Figure 1. Schematic of the test method.

A sample of concrete is placed between reservoirs of sodium chloride and sodium hydroxide and a voltage is applied and the current measured over a 6 hour period. This paper presents a computer model which is intended to describe the test.

The main objectives of the work are:
a. To make use of the shape of the current-time transient which is recorded every time the test is carried out.
b. To enable the test to differentiate between different factors which might cause higher charges to be recorded. For example a sample with a low initial concentration of hydroxyl ions might give a low result and be confused with a sample with a low chloride diffusion coefficient.
c. To obtain the chloride diffusion coefficient from the test to permit comparison with other tests.
d. To provide a scientific explanation for the results from the test.

2. The Physical Processes

2.1 The transport processes.
The significant transport processes which take place during the test are diffusion and electromigration.

In the diffusion process the dissolved ions move through the water at a rate determined by the concentration gradient. The flow per second per unit cross sectional area of the solid (the Flux, J) is given by Fick's law (3) which is shown in equation [1].

$$J = \varepsilon D \frac{dC}{dx} \quad mol/m^2/s \qquad [1]$$

where
ε is the porosity,
D is the intrinsic diffusion coefficient in m^2/s and
C is the ionic concentration in the pore fluid in mol/m^3.
x is the distance in m.

Electromigration is caused by the applied voltage. If an electric field is applied across the solid the negative ions will move towards the positive electrode (3).

The flux due to electromigration is given by equation [2]:

$$J = \frac{\varepsilon DzECF}{RT} \qquad mol/m^2/s \qquad [2]$$

where
z is the valency of the ion
F is the Faraday constant = 9.65×10^4 Coulomb/mol
E is the electric field in volts/m
R = 8.31 J/mol/^{o}K
T is the temperature in ^{o}K

2.2. Adsorption
The transport processes are restricted by adsorption in which a linear isotherm is assumed, i.e. a fixed proportion of the ions in any part of the barrier are adsorbed onto the matrix and will not move. To describe these processes two different ionic concentrations must be defined (4):

C kg/m^3 is the concentration of ions per unit volume of liquid in the pores. These ions will pass through the barrier under the influence of the physical transport processes. The concentration per unit volume of the solid will be ε C where ε is the porosity.

Cs kg/m^3 is the total concentration (including adsorbed ions) per unit volume of the solid. The ions which are adsorbed onto the solid will not move. The capacity factor is defined as [3]

$$\alpha = \frac{C_s}{C} \qquad [3]$$

The apparent diffusion coefficient D_a, which is measured if total concentrations rather than solution concentrations are measured, is related to the intrinsic diffusion coefficient by equation [4]

$$\frac{\alpha}{\varepsilon} = \frac{D}{D_a} \qquad [4]$$

2.3 Voltage Correction

The flux in equation 2 has a term in it for the electric field E. This will arise both from the applied voltage and the distribution of charged ions in the sample.

The field caused by the applied voltage will be uniform across the sample. At the start of the experiment all of the ions will be in pairs with no net charge but as soon as, for example, a chloride ion migrates into the sample without its sodium pair it will create a field E which will cause a potential difference (5) given by equation [5]

$$V = \int E\, dx \qquad Volts \qquad [5]$$

This will distort the uniform voltage drop caused by the applied potential.
This effect may also be explained in terms of resistances. The ends of the sample will be populated by different ions with different mobilities. This will give rise to different sample resistivities as shown in figure 2.

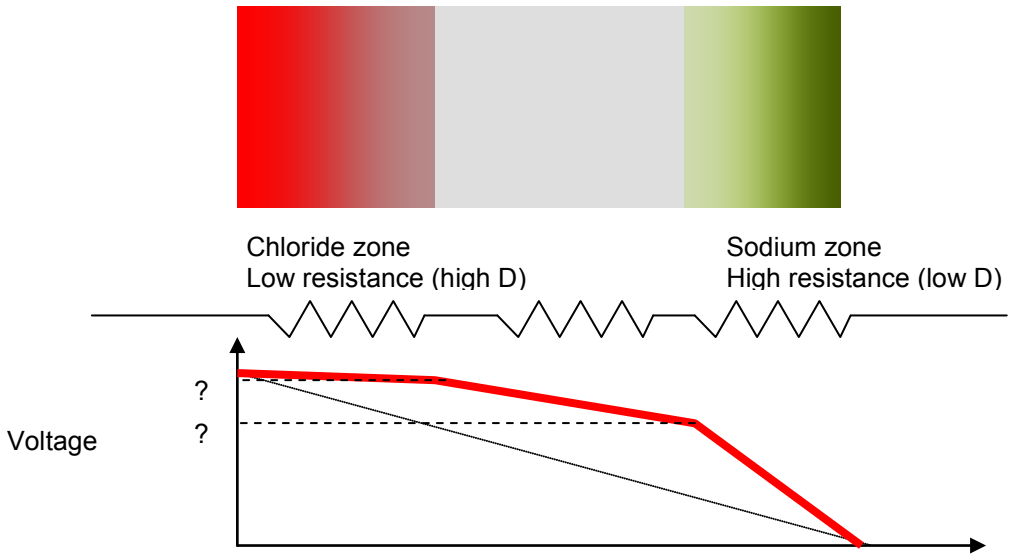


Figure 2 The cause of the voltage distortion explained in terms of resistances..

The effect of the field will be to inhibit further migration of ions causing any more build-up of charge. In this way Kirchoff's law will take effect and the current into any point within the sample will equal the current out of it. In the solutions at either end of the sample neutrality will be maintained by ion generation and removal at the electrodes.

The change in voltage will be a direct effect of different ionic concentrations in the sample. Soon after the start of the test there will be chloride ions in one side of the sample and sodium in the other side. The regions with these ions in them will have different resistivities due to the different mobilities of the different ions thus the system is equivalent to three different resistances in series. The voltage drop will depend on the size of each resistance and will not be uniform across the sample.

At the start of the test there is assumed to be virtually no chloride in the sample. When the voltage is applied the chloride ions will start moving into it. If they are to be responsible for the measured current they will be moving without the sodium anions. The rate at which they can flow in will be determined by the number of charge carriers (primarily hydroxyl ions) already available in the sample to carry the current forward to the anode. This concentration of existing charge carriers may be measured as the resistivity of the sample as discussed above. Clearly if there are no existing charge carriers in the sample (i.e. it is an insulator) no current will flow and chloride will only penetrate by diffusion.

Yu et al. (6) have carried out experimental measurements of ionic diffusion at an interface between chloride-free and chloride-containing cementitious materials. They observed that the chloride ions obeyed Fick's law but the hydroxyl ions distributed themselves to preserve charge balance. This

movement would have been cause by an electric field established by the chloride ions and is the mechanism proposed in the present work.

2.4 Temperature Calculation
When the current flows it will cause Ohmic heating in the sample. This is regularly observed during the experiments. The heat will be lost at a rate which is approximately proportional to the temperature difference between the sample and room temperature.

3. The computer model.

3.1 Transport Calculations.
The model works by repeated application of equations 1 and 2 through time and space. The sizes of the steps of time and space are set by continuously reducing them and checking that the solution remains constant. In particular the time step is reduced sufficiently to ensure that the concentration does not change by more than 10% during any time step. The calculations are carried out for ions in solution and at the end of each time step they are re-distributed using the capacity factor to calculate adsorption.

3.2 Voltage changes.
These effects are applied within the model by distorting the voltage and checked by ensuring that charge neutrality is maintained throughout the sample at all times. The sequence is shown in figure 3. This is clearly not possible if only one ion type is being considered and all therefore of the migrating ions are considered together. The initial concentrations in the sample must be equal for anions and cations and if the data does not comply with this requirement the model will not run. Final adjustments are made in each time step to ensure that the total voltage across the sample is correct.

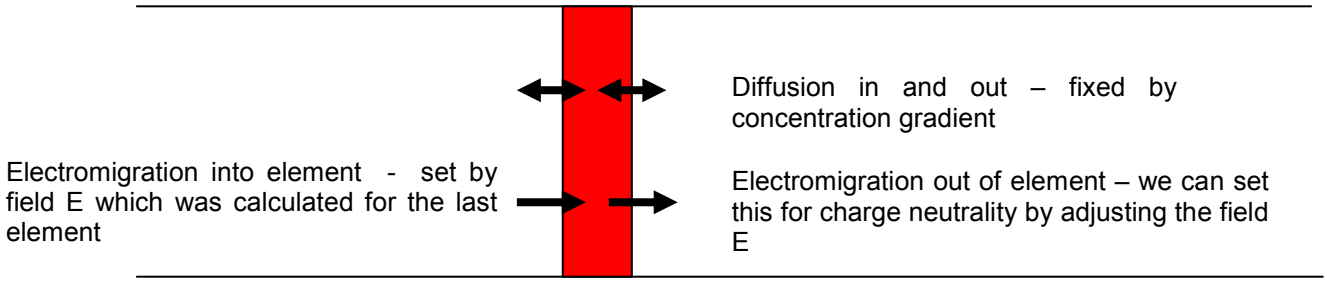


Figure 3. The sequence of the voltage correction in the computer model

Ion generation and removal at the electrodes is represented in the model by assuming that the ions being generated and removed are always hydroxyl ions. This assumption is probably most accurate at the cathode. At the anode some corrosion of the electrode will occur but checks on the sensitivity of the model have shown that this will not be a significant error.

3.3 Temperature
This effect has been included in the code with a constant of proportionality for the heat loss which was determined from experimental observations of the peak temperatures.

3.4 Optimisation.
The model which is outlined above would be useful for calculating the current transient for a sample for which all of the physical properties were known. In practice the opposite is required; the current transient is observed and the properties of the sample must be calculated from them. This can be done by a process of optimisation. Repeated modelling is carried out and the properties are adjusted to give a transient which is as close to the experimental values as possible. Unfortunately the properties cannot be considered sequentially for this. For example it is not possible to optimise the chloride diffusion and then go on to optimise the hydroxyl ion concentration because this will give a different minimum for the chloride diffusion. Thus the different properties must be optimised together.
The optimisation has been the process which has delayed the use of this model. The author previously presented the basic method (7) but was unable to apply it due to the limited capacity of the computers generally available at the time. With a modern standard desk-top computer three properties may be

optimised in a few hours. This may be seen as locating a single minimum point in the three dimensional space created by these three variables.

3.5 Methods used in the work presented in this paper.
For the work that is presented here the migration of four ions has been considered: chloride, hydroxyl, sodium and potassium. Each of these is defined by three variables, a diffusion coefficient, a capacity factor and an initial concentration in the sample. It has been noted above that the computers which were used were capable of optimising three of the resulting 12 variables which define the system. In effect nine variables must be set and the remaining three are calculated. For the present work the hydroxyl and chloride diffusion and initial concentration of hydroxl ions were optimise. Table 1 shows the initial values of the variables.

Table 1. Values for variables at start of run in base case prior to optimisation to fit experimental data.

Ion	Valence z	Intrinsic Diffusion Coefficient D m^2/s	Concentration C mol/m^3 (in liquid) negative reservoir	in sample	positive reservoir	Capacity Factor
hydroxyl	-1	1.65E-10	0	275	300	0.2
chloride	-1	6.00E-10	500	0	0	2
sodium	1	4.00E-10	500	138	300	0.2
potassium	1	9.00E-11	0	137	0	0.2
anion	1	0	0	0	0	0.1

When the initial concentration of one ion in the system was increased in order to optimise the solution it was necessary to balance this with a counter-ion to maintain neutrality. When the chloride was increased the counter-ion was assumed to be sodium but when the hydroxyl was increased an immobile anion was introduced to represent a net charge on the matrix.

Model Validation.

The model was validated by disabling the voltage corrections and confirming that the current-time transients agreed with analytical solutions to equations (1) and (2).

Experimental methods.
Mixes were cast to the proportions shown in Table 2 and cured in water for 28 days.

Table 2: Mixes used for experimental work

Mix	GGBS/cement	Water/cementitious	Sand/cementitious	Superplasticiser/cementitious
A	-	0.7	1.5	-
B	0.25	0.3	2.6	0.013

The testing was carried out using apparatus which was similar to that described in ASTM but with the following specific differences:
1. The end-volumes were larger at 0.8 litres, compared with typical volumes of 0.2 litres for the standard apparatus.
2. The experiment was run at 40 Volts.
3. The samples were run for 1000 minutes (17 hours). These longer runs typically give far greater changes in current during the test than are normally observed during a six hour test.
4. The cells were designed to give access to the top of the sample (8). For some samples this was used to establish a salt bridge by drilling 4mm diameter holes in the samples and installing a flexible plastic pipe containing 0.1M potassium chloride. The other end of the pipe was placed in a beaker with a reference electrode.
The computer modelling was carried out using code written in Visual Basic running as a macro in Microsoft Excel on a standard desk-top computer.

Results.

Typical results are shown in figures 4-6

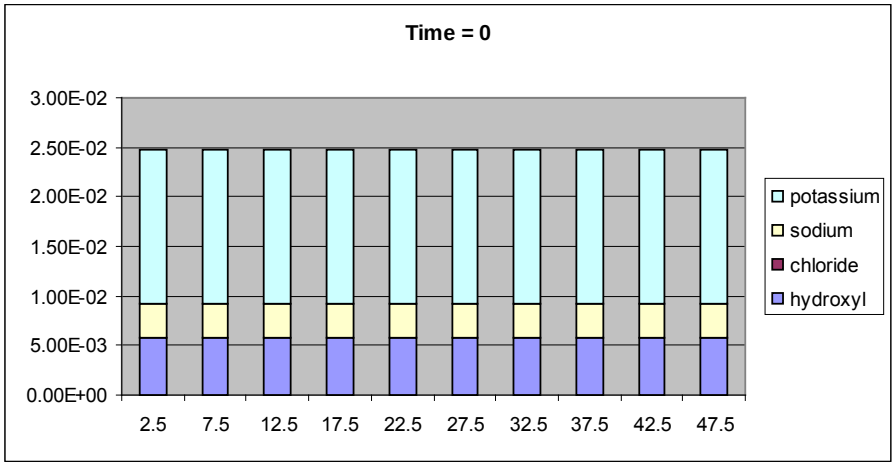


Figure 4. Current vs position at start of test

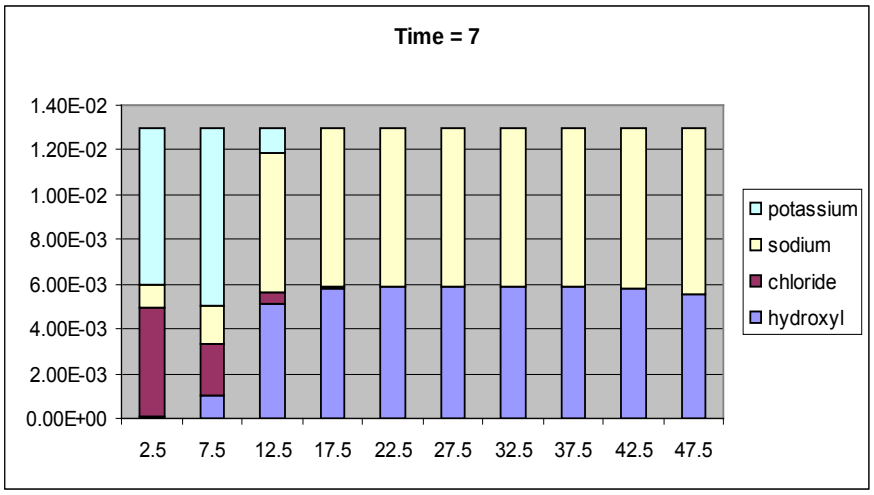


Figure 5. Current vs position at 7 hours

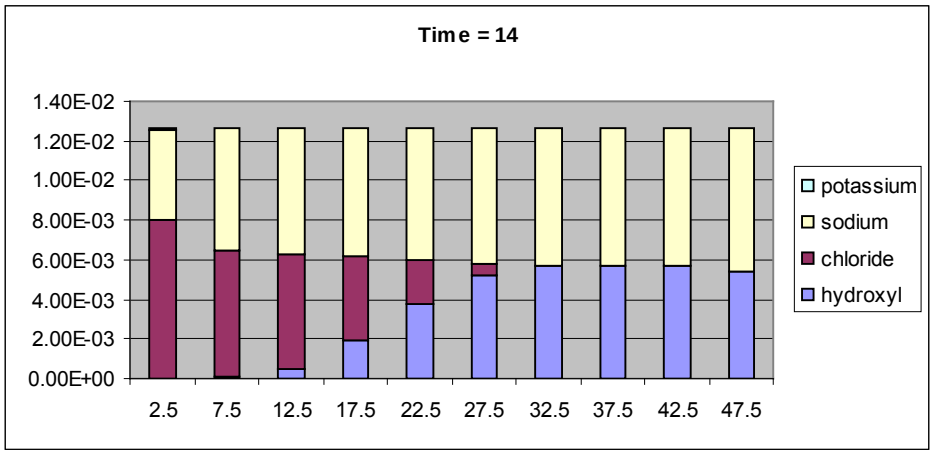
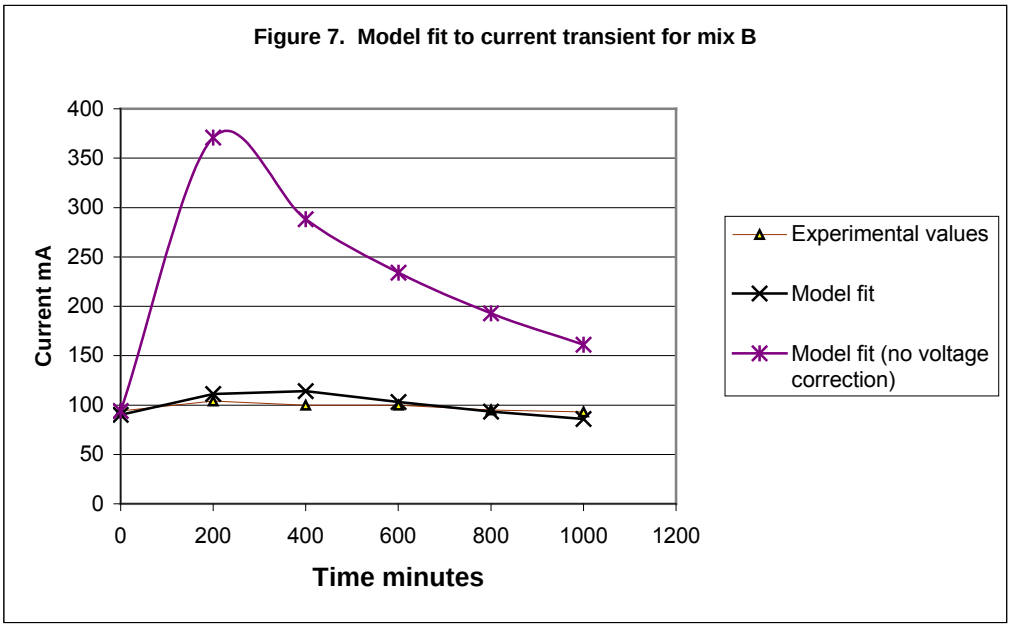


Figure 6 Current vs position at end of test.

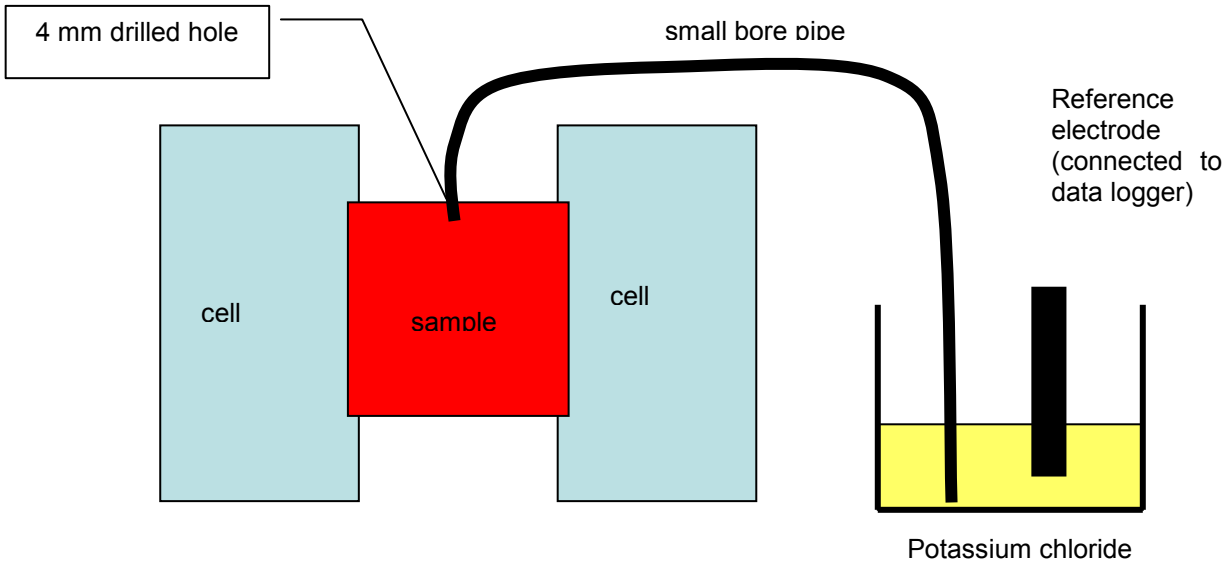
The key point about these results is that,the total current is the same at all positions in the sample. This is a requirement of Kirchoff's law. Figure 7 shows a current-time transient and illustrates ver clearly the significance of voltage correction.

Figure 7. Model fit to current transient for mix B



The voltage correction may be measured using a salt bridge as shown in figure 8

Salt bridge measurements



Results from these measurements together with modelling output are shown in figure 9.

Figure 9. Experimental and theoretical voltage distribution for mix B

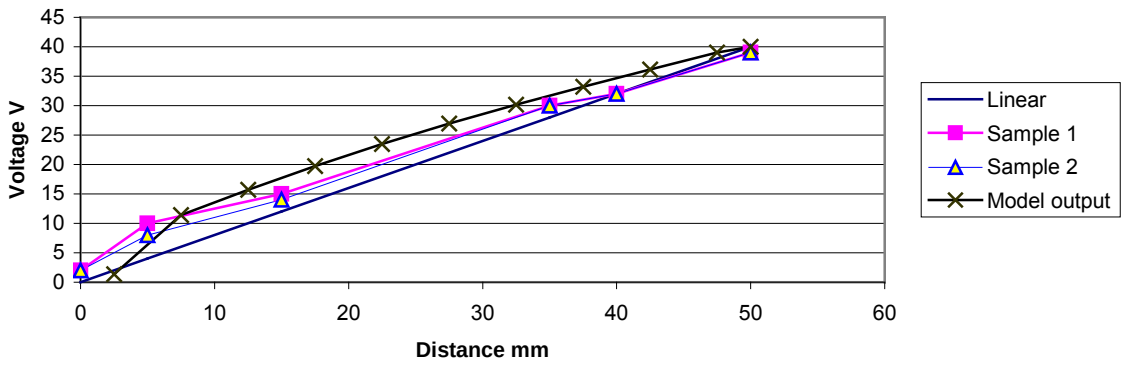


Figure 10 shows the predicted effect of variations in mid-point voltage on different parameters and indicates that this measurement would give very useful information about the sample.

Figure 10. Predicted effect on mid-point voltage of varying different parameters.

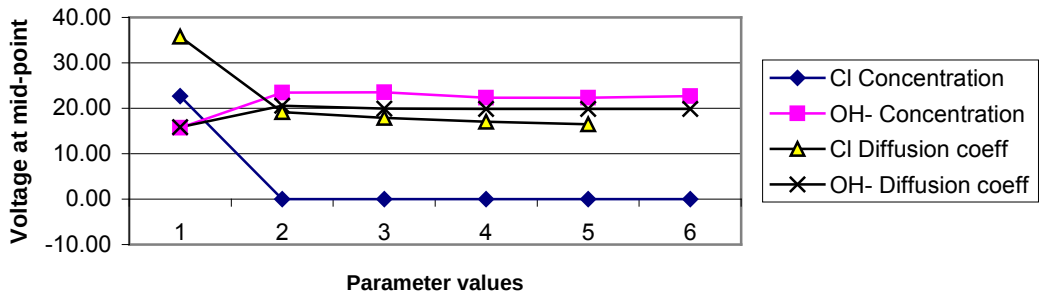
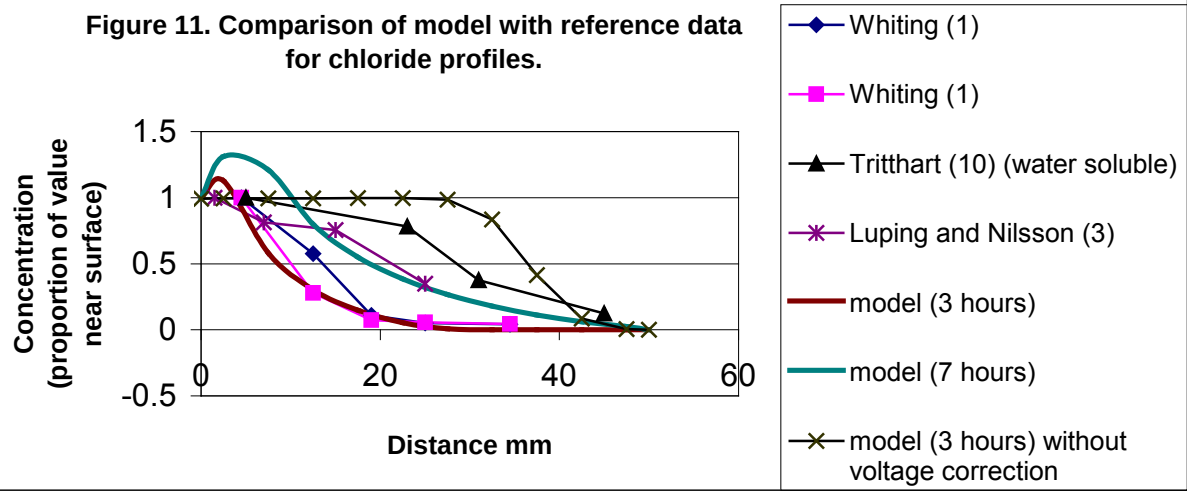


Figure 11 shows chloride profiles from several reference sources compared with results from the model.

Figure 11. Comparison of model with reference data for chloride profiles.



Stanish et al () have published papers describing a novel method for describing chloride ion transport due to an electrical gradient in concrete. In their paper they refer to the “abrupt” chloride front shown in the figure as being the result obtained without voltage correction. They then conclude that the more gradual transition indicated by the observed data must be caused by a novel dispersion mechanism related to the

porous structure of concrete and not adequately described by classical theory. The results from the present model shown on the graph show that they may be fully explained by the classical theory used in the computer simulation.